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March 1980

Fuel Gas Production from Animal and Agricultural Residues and Biomass

14th Quarterly Coordination Meeting January 30-February 1, 1980 Palo Alto, California

D. E. Jantzen
Biomass Program Office

SERI

Solar Energy Research Institute
A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401

Operated for the
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NOTICE

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UC CATEGORY: UC-61

FUEL GAS PRODUCTION FROM ANIMAL AND AGRICULTURAL RESIDUES

14th QUARTERLY PROGRESS REPORT

D. E. JANTZEN
BIOMASS PROGRAM OFFICE

MARCH 1980

PREPARED UNDER TASK NO. 3335.04

Solar Energy Research Institute

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FOREWORD

The 14th quarterly coordination meeting of the Anaerobic Digestion group of contractors working for the Biomass Energy Systems Branch, U.S. Department of Energy, was held in Palo Alto, California, Jan. 30-Feb. 1, 1980. The meeting included presentations of progress reports by the contractors, four invited presentations by groups working in similar research areas, and a tour of the Stanford University laboratories.

Dan Jantzen
Biomass Program Office
Solar Energy Research Institute

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LIST OF ATTENDEES
ANAEROBIC DIGESTION CONTRACTOR COORDINATION MEETING

Palo Alto, California
January 30 - February 1, 1980

ORGANIZATION	NAME	TELEPHONE
Cornell University 202 Riley - Robb Hall Ithaca, NY 14853	William J. Jewell	(607) 256-4533
Dynatech R/D Company 99 Erie Street Cambridge, MA 02139	Edward Ashare Don Wise	(617) 868-8050
University of Illinois Department of Civil Engr. Urbana, IL 61801	John Pfeffer	(217) 333-6965
Hamilton Standard Division United Technology Corp. Windsor Locks, CT 06096	Dan Lizdas Warren B. Coe	(203) 623-1621
University of Missouri Department of Chemical Engr. Rolla, MO 65401	J. L. Gaddy	(314) 341-4460
Solar Energy Research Institute 1617 Cole Boulevard Golden, CO 80401	Dan Jantzen	(303) 231-1469
Stanford University Department of Civil Engr. Stanford, CA 94305	Perry L. McCarty Lily Young	(415) 497-3504
U.S. Dept. of Agriculture Meat Animal Research Center P.O. Box 166 Clay Center, NE 68933	Andy Hashimoto	(402) 762-3241
Institute of Gas Technology 3424 State Street Chicago, IL 60616	David Chynoweth	(312) 567-3715
General Electric Company 751 Vandenburg Dr. King of Prussia, PA 19406	John Forro	
USDA Science and Education Admin. Western Regional Research Center 800 Buchannan Street Berkeley, CA 94710	Marcus Hart George O. Kohler	
Gas Research Institute 10 W. 35th Street Chicago, IL 60616	Jim Frank	(312) 567-6642

General Electric Company C/O Global Marine Development, Inc. 2302 Martin Street Irvine, CA 92715	Arnie Bryce	(714) 752-5050
Systems Technology Corp. 245 North Valley Road Xenia, OH 45385	Joe Swartzbaugh	(513) 372-8077
PRC Energy Analysis Co. 7600 Old Springhouse Rd. McLean, VA 22102	Ekkehart Gasper	(703) 893-1821 ext. 2425

AGENDA
ANAEROBIC DIGESTION CONTRACTOR COORDINATION MEETING

January 30-February 1, 1980
Palo Alto, California

Wednesday, January 30, 1980

7:00 - 7:15 p.m.	Introduction and Announcements Dan Jantzen, Perry McCarty
7:15 - 8:00 p.m.	A. G. Hashimoto USDA Meat Animal Research Center
8:00 - 8:45 p.m.	J. L. Gaddy University of Missouri
8:45 - 9:30 p.m.	P. L. McCarty Stanford University

Thursday, January 31, 1980

8:30 - 9:15 a.m.	W. J. Jewell Cornell University
9:15 - 10:00 a.m.	D. J. Lizdas, W. B. Coe Hamilton Standard
10:00 - 10:15 a.m.	Coffee Break
10:15 - 11:00 a.m.	J. T. Pfeffer University of Illinois
11:00 - 11:45 a.m.	E. Ashare (Crop Residue Feasibility Study) Dynatech R/D Company
11:45 - 1:45 p.m.	Lunch
1:45 - 2:30 p.m.	GE/GRI/WRRC/IGT (A. J. Bryce; David Chynoweth)
2:30 - 3:15 p.m.	GE/GRI/WRRC/IGT (John Forro)
3:15 - 3:30 p.m.	Coffee Break
3:30 - 4:15 p.m.	J. Swartzbaugh Systems Technology Corporation
4:15 - 5:00 p.m.	D. L. Wise (Biomethanation) Dynatech R/D Company
6:15 p.m.	Dinner - Stanford Faculty Lounge

Friday, February 1, 1980

8:30 - 9:30 a.m.	Policy, contractual arrangements, etc. Dan Jantzen
9:30 - 9:45 a.m.	Coffee Break
9:45 - 11:30 a.m.	Perry McCarty (Tour of Stanford University Labs)

ANAEROBIC FERMENTATION OF LIVESTOCK AND CROP RESIDUES

QUARTERLY PROGRESS REPORT
SEPTEMBER to DECEMBER, 1979

A. G. HASHIMOTO
Y. R. CHEN

ROMAN L. HRUSKA U.S. MEAT ANIMAL RESEARCH CENTER
AGRICULTURAL RESEARCH
SCIENCE AND EDUCATION ADMINISTRATION
U.S DEPARTMENT OF AGRICULTURE
CLAY CENTER, NEBRASKA 68933

PREPARED FOR

U.S. DEPARTMENT OF ENERGY
DIVISION OF SOLAR TECHNOLOGY
BIOMASS ENERGY SYSTEMS BRANCH
INTERAGENCY AGREEMENT DE-AI01-79ET20638

INTRODUCTION

The overall objective of this project is to evaluate the technical and economic feasibilty of the anaerobic fermentation process to recover methane and high protein biomass from beef cattle and crop residues. The specific objectives of interest to the Department of Energy are: a) to develop design criteria for optimum production of methane from anaerobic fermentation of beef cattle and crop residue; and b) to determine the capital and operating costs, and energy, manpower and safety requirements for anaerobic fermentation systems associated with livestock operations. This report summarizes the operation of the pilot-scale fermenter during the reporting period.

PILOT-SCALE FERMENTER

At the end of the last reporting period, we were attempting to operate the fermenter at a 6 day retention time, influent volatile solids concentration of 100 g/L and temperature of 50° C. We were not able to maintain stable operation under these conditions, so the influent concentration was reduced to allow the fermenter to stabilize. After several weeks, the influent concentration was increased to 80 g VS/L and steady-state was achieved. Table 1 summarizes the operating parameters of the fermenter at 50° C and 6 days retention time. The results show that about 48% of the volatile solids is reduced and that the other parameters closely follow the results presented previously for the pilot-scale fermenter operating at 55° C.

Unlike the previous reporting period where we obtained lower than predicted CH_4 production rates and yields due to gas leaks, the present results indicate a higher than expected rate and yield. A yield of 0.60 L CH_4/g VS used is about 15% higher than our previous results and a rate 3.84 L CH_4/L· day is also about 15% higher than would be predicted assuming our previously reported kinetic equation and $_m$ = 0.52 day^{-1} at 50° C, B_o = 0.35 L CH_4/g VS fed and K = 0.9. The reason for the higher CH_4 production rate and yield is being investigated.

FUTURE ACTIVITIES

Complete experiments using beef manure as substrate and initiate experiments on crop residue and manure mixtures as substrate.

Table 1. SUMMARY OF STEADY-STATE OPERATING PARAMETERS FOR THE PILOT-SCALE FERMENTER[a]

Parameter	Temperature/Retention Time 50°C/6 day
Total Solids	
Inf., g/L	92.0 ± 3.1
Eff., g/L	53.8 ± 5.6
Change, %	-41.5
Volatile Solids	
Inf., g/L	80.2 ± 2.9
Eff., g/L	42.1 ± 0.5
Change, %	-47.5
Fixed Solids	
Inf., g/L	11.8
Eff., g/L	11.7
Change, %	-0.8
COD	
Inf., g/L	94.3 ± 5.2
Eff., g/L	56.5 ± 5.5
Change, %	-40.1
Amonia-N	
Inf., g/L	1.23 ± 0.05
Eff., g/L	1.49 ± 0.02
Volatile Acids	
Inf., g/L	6.41 ± 1.38
Eff., g/L	1.68 ± 0.07
Alkalinity	
Inf., g/L	5.05 ± 0.38
Eff., g/L	10.23 ± 0.34
pH	
Inf.	5.44 ± 0.22
Eff.	7.91 ± 0.06
Methane, %	59.4 ± 0.7
Methane Production	
L/L·day	3.84
L/g VS added	0.29
L/g VS utilized	0.60
L/g COD utilized	0.61

[a]Data presented as mean ± standard deviation, steady-state assumed after four retention times

ECONOMIC AND KINETIC STUDIES OF THE PRODUCTION OF CHEMICALS AND FARM ENERGY BY FERMENTATION OF BIOMASS

SERI Contract No. XJ-9-8020-1

Quarterly Report for Period 11/1/79 - 2/1/80

J.L. Gaddy
University of Missouri
Rolla, Missouri

The objectives of this project are twofold:

a) Determine the technical and economic feasibility of producing farm energy by anaerobic digestion of agricultural residues and native grasses.

b) Investigate improvements in kinetics or yield and production of other products by separation of the steps of the anaerobic digestion process.

FARM ENERGY SYSTEM

Mechanical agitators for the four farm reactors are being modified for reciprocating action with pneumatic cyliners on each tank. Two of the reactors have been restarted, one with hay concentration of 5.5 percent and the other with 7.2 percent hay. Inoculum was with .5 percent sewage sludge and effluent from older cultures. Start up went smoothly with infrequent lime additions needed during the first week to maintain pH $\geq$ 6.8.

The performance of Reactor 4 (5.5 percent hay) is shown in Figure 1. Gas production started immediately and reached a maximum of around 400 cubic feet per day during the first ten days. Production remained above 100 cubic per day for five weeks. Methane concentration was consistently above 50 percent. The carbon destruction reached 30 percent in 36 days and about 40 percent in eight weeks.

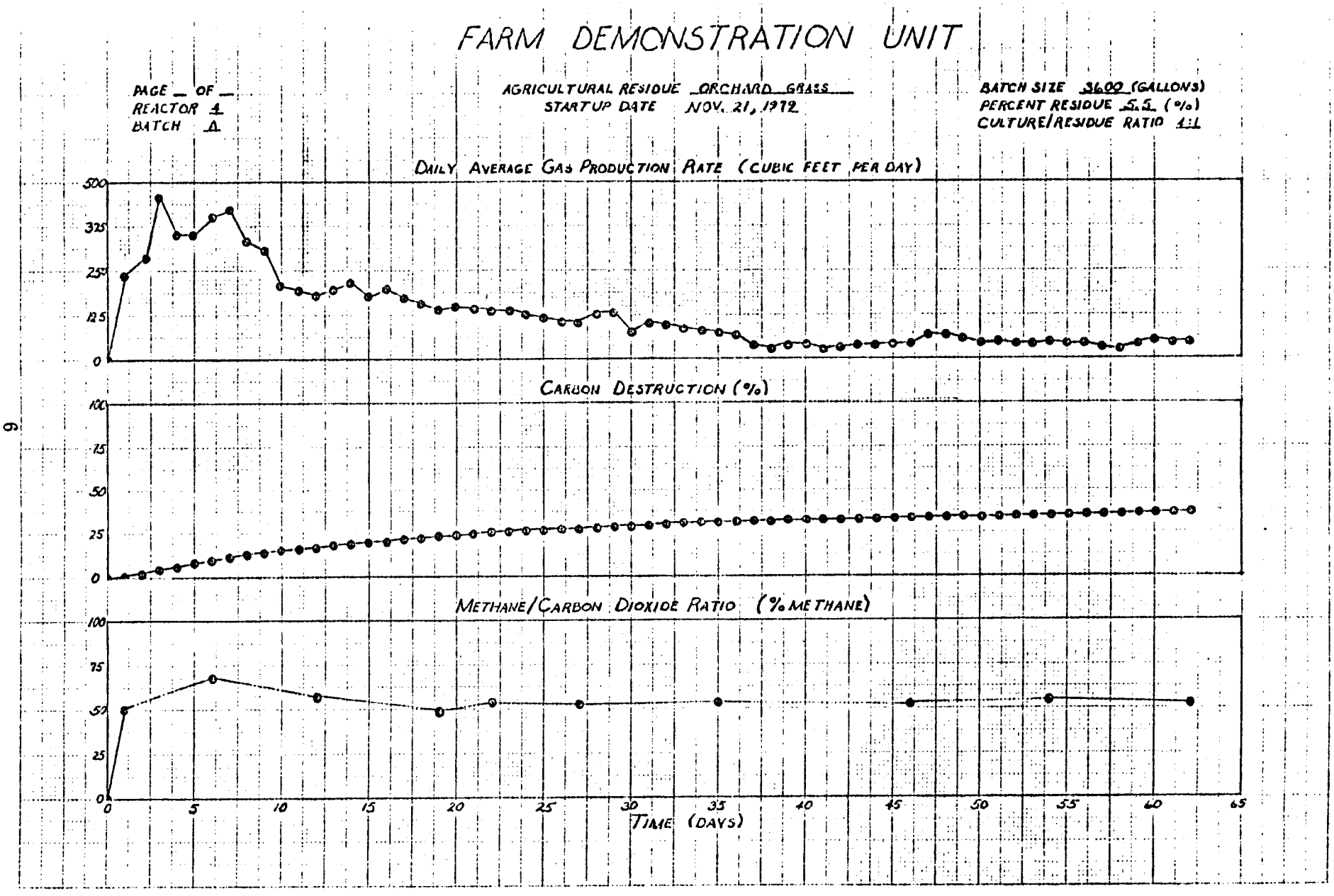

Figure 1. Reactor Operating Performance

Operation of the new agitators has been satisfactory. Agitation is periodic with operation for a few minutes twice per day. Modification of the agitators in the other two reactors is underway and operation at full capacity is expected soon. Second cycle operation will be with 10 percent hay.

Laboratory batch reactors are being operated to test nutrient and inoculum levels and to provide guidance for the farm system. Figure 2 shows the performance of a laboratory batch culture for four 60 day cycles. These reactors are using hay from the farm. Operation is with 10 percent hay and inoculum is from the previous cycle using four parts mixed effluent to one part dry hay. Maximum gas production is seen to occur within the first two weeks. No problems with pH control or gas composition have occurred in the eight month operation. Carbon destruction continues to improve with each cycle. Fifty percent conversion is achieved on completion of the fourth cycle. Nutrient deficiencies are not apparent with the 4/1 inoculum, although C/N_2 in the hay is about 50/1. Also, the cultures appear to get stronger with age, so that toxicity does not appear to be a problem.

Elemental analyses of the farm native grasses and reactor effluent have been conducted. A summary of available nutrients is given in Table 1. Each ton of effluent returned to an acre of grassland would contain 32.8 lb N_2 and 11.6 lb P. Toxicity tests have also been conducted with this effluent material. The results of the germination tests with various crops are given in Table 2. These results indicate that the effluent is non toxic to these plants even at reasonably high application rates.

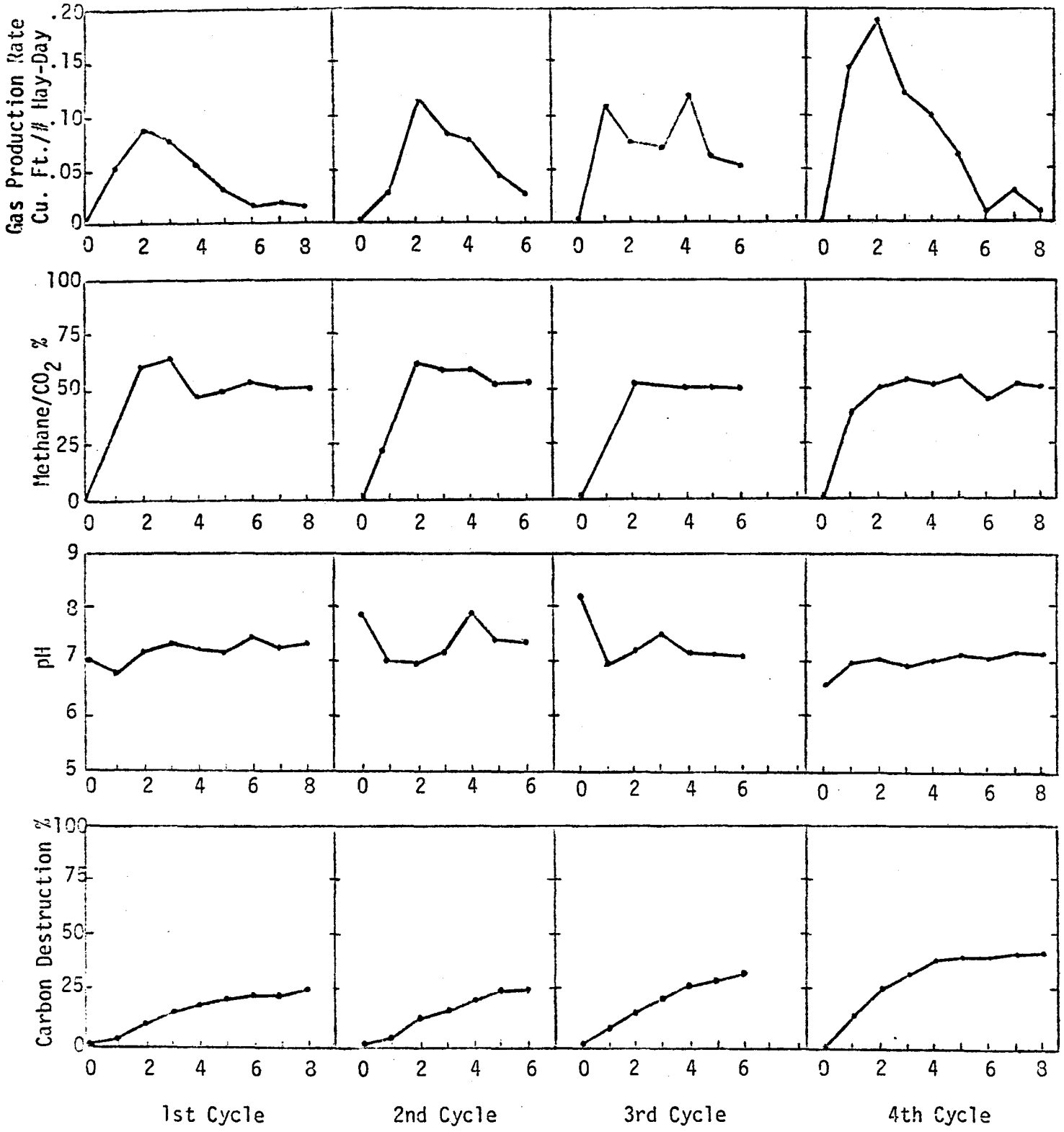

Figure 2. Laboratory Digestor Performance

Table 1. Amounts of various nutrients added with methane generator sludge.

Quantity added* g sludge Kg soil	N	P	K	S	Na	Mg	Ca	Mn	Zn	Fe
	mg nutrient/Kg of soil sludge mixture									
10	164	58	35	32	17	23	660	3	3	32
20	328	115	70	64	33	46	1320	6	6	63
40	656	230	140	128	66	92	2640	12	12	126
80	1312	460	280	256	132	184	5280	24	24	252

* Note that for approximate usage g/kg is often noted as Tons/acre.

Table 2. Germination of various seeds in Menfro soil amended with methane generator sludge.

Quantity added	Crop Type	Number Planted	Germinated
g/sludge/Kg soil			%
0	corn	38	84
10		40	85
20		40	80
L.S.D. (0.95)			20
0	alfalfa	164	42.
20		200	38
80		180	37
L.S.D. (0.95)			16
0	soybean	56	78
40		54	72
80		56	82
L.S.D. (0.95)			15

ACID HYDROLYSIS/FERMENTATION STUDIES

Hydrolysis of biomass with sulfuric acid produces a mixture of sugars which can be fermented to acids, alcohols, methane or other products. A two step hydrolysis has been found to give good yields with little sugar decomposition and low acid utilization.

The first step uses dilute acid for conversion of hemicellulose to xylose. The residual solids are contacted with concentrated acid in the second step where cellulose is converted to glucose.

Parameters affecting the yield and rate of hydrolysis are acid concentration, temperature and time of contact. High acid concentrations and temperatures increase the conversion rate, but also speed up the decomposition of sugars to furfurals and other undesirable by-products, thereby decreasing yields. Therefore, an optimal set of parameters is sought that will maximize the yield and reaction rate. Best conditions for the prehydrolysis appear to be an acid concentration of 4.4 percent and a temperature of 98°C. For the hydrolysis, the optimal conditions are about 85 percent acid with a temperature of 100°C.

Table 3 gives the results of hydrolysis of orchard grass and corn stover using these procedures. The prehydrolysis produces a mixture of xylose and glucose. However, the hydrolysis produces primarily glucose, indicating good conversion of hemicellulose in the prehydrolysis. Combined yields are about 90 percent hemicellulose and cellulose to sugars.

A two step fermentation of the orchard grass sugars to methane has been investigated. The first step is a mixed culture of acid forming bacteria obtained from a sewage sludge culture. The second step is a mixed culture of methane bacteria, also from sewage sludge.

Table 3. Acid Hydrolysis Data

	Orchard Grass	Corn Stover
Prehydrolyzate		
Xylose, g/l	11.1	7.7
g/100g	18.5	13.1
Glucose, g/l	14.3	2.2
g/100g	23.8	3.2
Hydrolyzate		
Xylose, g/l	3.2	
g/100g	1.8	
Glucose, g/l	39.4	39.4
g/100g	22.5	29.5
Combined		
Xylose, g/100g	20.3	13.1
Glucose, g/100g	46.3	32.7

The two step conversion yields a maximum of 5 cubic feet of methane per pound of orchard grass fed, compared to a maximum of 2.3 for a single stage culture. Reaction rates for the separate steps are also somewhat faster. However, preliminary economics show that the single stage conversion is preferred due to the high cost of base to adjust pH into the methane reactors. Studies are to be conducted utilizing the sugars from corn stover hydrolysis in a single mixed acid and methane culture.

Stanford University
Department of Civil Engineering

HEAT TREATMENT OF ORGANICS

FOR

INCREASING ANAEROBIC BIODEGRADABILITY

Contract SERI XR-9-81-74-1

QUARTERLY PROGRESS REPORT

for the period

October 1, 1979 to December 31, 1979

by

D. Stuckey, P. J. Colberg, K. Baugh, T. Everhart, D. Harrison,
L. LaPat, L. Y. Young, and P. L. McCarty

Prepared for

Solar Energy Research Institute

1536 Cole Boulevard

Golden, Colorado 80401

January 30, 1980

I. INTRODUCTION

The objective of this study is to evaluate thermochemical pretreatment as a method for increasing the anaerobic biodegradability of organic materials so that they can be more completely fermented to methane gas, a potential source of fuel. The current study has five specific phases: (1) biological conversion of lignocellulose to methane, (2) biodegradation of lignin and lignin fractions, (3) pretreatment of nitrogenous organics for increasing biodegradability, (4) biodegradation of lignin aromatic compounds, and (5) biochemical methane potential and toxicity testing.

Results are reported for phases one through three. Phase four is completed, and no new information is available for phase five at this time.

II. BIOLOGICAL CONVERSION OF LIGNOCELLULOSE TO METHANE

K. Baugh, T. Everhart, A. Bachmann, D. Harrison, and P. L. McCarty

A. BACKGROUND

Staged thermal treatment of milled white fir, a representative difficult to biodegrade lignocellulosic material, has been shown to increase the production of biodegradable materials through the solubilization of the carbohydrate fraction of the wood matrix (Owen and McCarty, 1979, Baugh and McCarty, 1979). This process, which does not require added chemicals, is termed staged autohydrolysis. It shows promise for significantly increasing biodegradability to methane and is being explored in detail. Studies currently underway include three areas: (1) the effect of treatment variables on cellulose solubilization, (2) characterization of organic products formed, and (3) anaerobic treatment of soluble products. Progress in each of these different areas since the previous

quarterly report is described in the following.

B. EFFECT OF TREATMENT VARIABLES (K. Baugh and D. Harrison)

Treatment in the first phase to 200°C with immediate cooling, in the second and third phases at 225°C for two hours each produced a combined solubilized organic phase which contained approximately 50 percent of the initial wood chemical oxygen demand (COD), and an overall bioconversion efficiency referenced to initial feed of just over 30 percent. This compares to a COD solubilization of 22 percent (Owen and McCarty, 1978) at the maximum COD bioconversion efficiency of 16 percent when referenced to initial feed COD for single stage treatment (Owen and McCarty, 1979). Staged treatment under the above conditions has been conducted several times in order to evaluate reproducibility and also to provide solublized material for organic characterization. As soon as the organic analytical procedures have been standardized for quantification, the effect of other conditions of staged treatment will be evaluated.

C. CHARACTERIZATION OF ORGANIC PRODUCTS (T. Everhart and K. Baugh)

Since the previous quarterly report, analytical procedures for the characterization of the soluble organics obtained from the various stages of lignocellulose heat treatment have been under development. Four different gas chromatographic procedures are being applied, and each is designed to detect and quantify different clases of soluble organic compounds.

The first analytical procedure is used for determining volatile fatty acids (VFA). An aliquot of sample is acidified with concentrated sulfuric acid, and the VFA are extracted with ethyl ether. A sample of extract is injected onto a 6-foot glass column packed with 10% SP-1000/1% H_3PO_4 on 100/120 mesh Chromosorb WAW. Flame ionization is used for detection, and analyses are conducted isotermally at 150°C. Acetic acid is the major VFA found to date in samples from

autohydrolysis of wood.

The second procedure is used for the determination of furfurals, which are expected to be formed from thermal degradation of sugars formed from cellulose and hemicellulose hydrolysis. It is anticipated that the major product formed will be hydroxymethylfurfural, although other gas chromatographable and extractable hydrophobic organic compounds should also be determined by this procedure. An aliquot of sample is extracted with dichloromethane, and the extract is evaporated to dryness under nitrogen. A small quantity of dichloromethane is then used to redissolve the organics for injection splitless onto a 50 m UCON HB capillary column at 40°C. The temperature is then programmed at 3° C/min to 180°C. Eluting compounds are detected and analyzed either by FID or MS. In addition to the expected furfural and hydroxymethylfurfural, thirty-five other compounds were detected, including methylated and acetylated furans, methylated furfurals, aliphatic ketones, guaiacol, phenol, vanillin, and several other lignin derived organics yet to be identified.

The third procedure is being used for the determinatin of higher molecular weight (150-400) and more polar organic compounds, such as carboxylic acids and phenols. There are some overlaps between compounds detected by this and the second procedure. An aliquot of sample is acidified with concentrated hydrochloric acid, extracted with dichloromethane, and evaporated to dryness. The dry residue is redissolved in methanol and mixed with alcoholic-ethereal diazomethane for methylation. After drying, the sample is redissolved in 50/50 (V/V) ether/methanol and injected splitless onto a 50-m Se-52 capillary column at 70° C. The temperature is programmed to 300°C at 3°C/min. Detection and analysis is either with FID or MS.

A minimum of 75 different substances have been detected by the third

procedure, including phenols such as methylated guaiacol and vanillin, other higher derived materials such as methyl-3,4 dimethoxybenzoate and methyl ferulate, and fatty acid methyl esters such as methyl myristate, methyl palmitate, two methyl pentadecanoates, methyl stearate, methyl oleate and methyl linoleate, many unidentified aromatic acid methyl esters and neutrals, and many unidentified compounds with an MS base peak of 151, characteristic of methoxyphenones, which are definite ligin derived materials.

The last procedure, still under development, is used for the analysis of monosaccharide sugars (Schaleger and Brink, 1977). This involves the freeze drying of an aliquot of sample and resolubilization in a pyridine solution of hydroxylamine hydrochloride, followed by heating at 85°C for one hour. The monosaccharides are converted by this procedure to oximes which are then converted to aldononitrile acetates through subsequent steps of acetic anhydride addition and heating. A small aliquot is injected splitless onto the same column as for the third procedure at 140°C, and temperature programmed to 250°C at 3° C/min. Both FID and MS detection and analysis are also used. The method is almost developed and samples should be analyzed in the near future.

The methods are at present suitable for qualitative analysis, and will be developed futher for quantitative analysis of the compounds occuring in most significant concentrations.

D. ANAEROBIC TREATMENT OF AUTOHYDROLYSIS LIQUOR (A. Bachmann)

The above studies have shown that staged autohydrolysis of white fir increases biodegradability through solubilization of the organic constituents. The resulting soluble fraction is relatively low in concentration, generally 5 to 20 g/l, and for this reason would be uneconomical to treat by the conventional anaerobic treatment process. In addition, the soluble fraction contains

materials which are toxic to anaerobic microorganisms and it is not presently known whether this would limit continuous anaerobic treatment. Thus, the objective of this study is to investigate the feasibility of continuous anaerobic treatment of autohydrolysis liquor in contact reactors which permit methane fermentation at short detention times.

Three different contact reactors were chosen for study since each has good potential for treatment of dilute wastes at short detention time: the anaerobic filter, the anaerobic rotating biological contactor, and the anaerobic contact process. Each reactor is capable of maintaining a highly active population of microorganisms that is not removed from the system by the liquor as it passes through. This feature allows active methane fermentation at liquor detention times of one day or less. The anaerobic filter consists of a bed of stone through which the liquor is passed continuously in an upward direction. Anaerobic microorganisms become attached to the stone media or persist in the interstitial spaces between. The rotating biological contactor consists of slowly rotating circular plates within the reactor and connected to a horizontal shaft to which the microorganisms become attached. The liquor passes through in the horizontal direction and comes in contact with the microorganisms on the plates. In the anaerobic contact process, liquor flows in an upward direction through a suspension of microorganisms. The particular design encourages separation of microorganisms from the evolving gas and effluent liquor, thus keeping the microorganisms within the reactor. The latter reactor is the simplest and would be the least costly to build, but may not have the reliability of the other two. This important aspect of cost versus reliability will be studied.

To date the three reactors have been built (each with a capacity of 0.4

to 0.7 liters) and are presently operating at a 1 day detention time on a synthetic glucose-nutrient broth substrate having a COD of 8 g/l. In general, this results in 3 volumes of methane produced per day per volume of reactor. The next step, which has just begun, is the introduction of autohydrolysis liquor. This will be done slowly by mixing the liquor with the synthetic substrate and increasing the percentage of autohydrolysis liquor in the mixture by about 10 percent per week until 100 percent autohyrolysis liquor is being treated or else until inhibition to the system is noted.

Once continuous anaerobic treatment of autohydrolysis liquor is attained, then the particular organic compounds entering and leaving the reactor will be evaluated in order to determine which ones are biodegradable and which are not. If inhibition is found, then analysis may help to determine which compound or combination of compounds is the cause. Assuming satisfactory treatment results, then the three different reactors will be compared for relative efficiencies and reliability.

III. BIODEGRADATION OF LIGNIN AND LIGNIN FRACTIONS

P. J. Colberg, L. LaPat and L. Y. Young

A. INTRODUCTION

Volatile fatty acids (VFA) are known to be readily utilizable substrates for methanogenic bacteria. This report contains results of gas chromatographic (GC) analysis of enrichments resulting from the biochemical methane potential (BMP) testing of alkaline heat-treated peat, which consists largely of lignin. The BMP data were presented in the previous progress report (Stuckey et al., 1979). Samples were analyzed for the C_1 to C_7 volatile fatty acids according to the protocol of Healy et al., 1979.

B. RESULTS AND DISCUSSION

Our previous results (Stuckey, et al., 1979) indicated that the percent bioconversion of original substrate carbon to CO_2 and CH_4 was similar for different molecular-weight fractions of alkaline heat-treated peat. It was suggested that this may have been due to the degradation of the same compound(s) in each fraction, regardless of molecular size. Since the fractions were separated via gel filtration chromatography, these suspected compounds would also have to be unaffected by molecular sieving and be eluted indiscriminately with each fraction. Based on GC analysis for VFA, this group of potentially utilizable substrates fulfills these criteria. VFA were eluted in all three molecular weight fractions at similar concentrations. Thus, separation of these compounds according to molecular weight was not achieved, which calls into question the previous indication that high molecular weight lignin fractions were as biodegradable as low molecular weight fractions.

The three fractions previously separated had average apparent molecular weights of 1400, 600, and 200, respectively. The VFA contents of each fraction are given in Table 1. Table 2 lists the VFA content of cultures after 30 days of incubation in the BMP test. In this test, seven different concentrations of each fraction were tested ranging from 100 mgC/l to 1500 mgC/l. From these results the following observations can be made:

1. Mass balances of the total organic carbon (TOC) of the volatile fatty acids indicate that there was a net increase in VFA carbon during incubation for fractions 1 and 2, while for fraction 3 there appears to have been a net decrease. The percentage change in TOC is indicated in the last column for each fraction. Also, there was a general absence of 1 to 3 carbon VFA after incubation which suggests that these acids were depleted during methane

TABLE 1. ORIGINAL VOLATILE FATTY ACID COMPOSITION OF ALKALINE HEAT-TREATED PEAT FRACTIONS (mgC/l)

Volatile Fatty Acid	Fraction 1 (2000 mgC/l)	Fraction 2 (2000 mgC/l)	Fraction 3 (2000 mgC/l)
C_1	Not Determined		
C_2	6.7	-	-
C_3	-	-	-
C_4	25	11.6	15.6
C_5	10.5	7.8	12
C_6	54	8	67
C_7	-	-	-
% TOC as VFA	4.8	1.4	4.7

- Compound not detected

TABLE 2. VOLATILE FATTY ACID (VFA) COMPOSITION OF ALKALINE HEAT-TREATED PEAT FRACTIONS AFTER 30 DAYS OF INCUBATION IN BMP TEST

Conc. of Sample Incubated mgC/l	Fraction 1 (MW-1400)								Fraction 2 (MW-600)								Fraction 3 (MW-200)							
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	Net Change in % TOC	C_1	C_2	C_3	C_4	C_5	C_6	C_7	Net Change in % TOC	C_1	C_2	C_3	C_4	C_5	C_6	C_7	Net Change in % TOC
100	-	-	-	120	-	50	70	7.2	-	-	-	214	44	-	-	11.5	-	-	-	-	-	-	-	-
300	-	-	-	73	-	257	271	25.5	-	-	-	128	40	4	-	7.3	-	19	3	9	1	-	-	-2.6
500	Sample not available								-	-	-	56	6	-	-	1.7	*	20	-	47	.3	-	-	-1.2
750	*	-	-	68	57	33	22	9.1	-	33	4	-	60	2	-	6.6	*	-	189	13	10	-	12	6.8
1000	*	-	-	48	102	22	-	6.6	-	9	-	66	178	-	10	11.7	-	-	-	27	-	-	-	-3.4
1200	*	1	-	33	71	2	-	2.0									-	8	-	15	-	-	-	-3.5
1500	*	3	-	44	118	-	6	0.7									-	-	-	5	-	-	-	-3.7

- Denotes compound was not detected.
* Eluted with solvent peak, not determinable.

fermentation over the 30-day incubation period. In the first two fractions there was a net increase in the higher VFA, while in the third fraction there was a net decrease and somewhat of a shift toward the shorter fatty acids.

2. The seeded BMP controls contained no detectable quantities of VFA. Therefore, the increases in VFA noted were the result of biodegradation and not due to background activity in the seed.

3. The overall percentage of TOC converted to CO_2 and CH_4 by each fraction during incubation averaged about 5 percent (Stuckey et al, 1979). However, the percent TOC converted to intermediate volatile acids varied considerably but with no distinguishable trends noted between the various substrate concentrations tested.

Based upon the chemical analysis of the alkaline heat-treated peat preparation (Owen, 1979), and assuming a mean TOC content equivalent to that of glucose, it is estimated that only 4 percent of the TOC of the unfractionated peat is carbohydrate. Since a greater percentage than this is represented by the accumulated VFA in fractions 1 and 2, there must have been additional sources of VFA, particularly among the higher molecular weight fractions.

From the structural models proposed for lignin (Adler, 1968), there appear to be two potential sources of VFA: (1) the intermonomer linkages; and/or (2) cleavage of the phenylpropanoid monomers. Breakage of the aryl-glycerol-p-aryl ether linkage during heat treatment or biological attack could release a C fragment almost identical to propionate. These C_3 fragments would readily be converted to methane. It is unclear at this time whether ring cleavage occurred. Some heptanoate (C_7), however, was detected and it has been reported as a ring-fission product of benzoate (Evans, 1977; Healy et al., 1979).

In summary, there appear to be several sources of VFA in these enrichments. The C_1 to C_3 VFA have three potential sources: (a) original carbohydrate in the substrate (4% of TOC); (b) stepwise degradation of original C_4 to C_7 volatile acids; and (c) fragments from intermonomer linkages. Because of the molecular size of fraction 3 (i.e. single-ring range) it is unlikely that intermonomer linkages would be a source of VFA. Rather the C_4 to C_7 VFA may result from (a) ring cleavage of phenylpropanoids (especially C_6 and C_7); (b) original carbohydrate in substrate; or (c) stepwise degradation of original VFA.

Work in progress utilizing ^{14}C-(LIGNIN)-lignocelluloses of high specific activity may help to determine more specifically both the origin and fate of VFA. In addition, technique development for application of high performance liquid chromatography (HPLC) to these studies is continuing.

IV. PRETREATMENT OF NITROGENOUS MATERIALS

D. C. Stuckey and P. L. McCarty

A. INTRODUCTION

The effect of thermochemical pretreatment on the biodegradability and toxicity of nitrogenous organics has been under study for the past four years, and is currently being concluded. Data obtained during the study has been presented in past reports, and hence the purpose of this report is to give a brief synopsis of past work together with final conclusions.

B. PRELIMINARY STUDIES

The overall study was conducted in four phases. The initial phase was a preliminary investigation as to whether pretreatment could enhance the biodegradability of two highly nitrogenous materials, waste activated and primay sludges from municipal wastewater treatment plants. These preliminary data

indicated that increases of 70 percent in bioconvertability to methane were obtainable with waste activated sludge (WAS), however, primary sludge seemed to be relatively unaffected. Data obtained also indicated that toxic compounds were produced during pretreatment which inhibited digester performance.

C. EFFECT OF PRETREATMENT VARIABLES

In the second phase questions raised by the initial phase were addressed such as the effect of pretreatment on the chemical composition of WAS and its toxicity, and the influence of chemical addition (NaOH, HCl and $Ca(OH)_2$) on both bioconvertability and toxicity. Low temperature (150°C) pretreatment appears to result in lysis of WAS, with the concomitant release of soluble organics. As the pretreatment temperature rose, bioconvertability increased, and reached an optimum of 68 percent at 175°C. Above this temperature there was a sharp decline, and only 43 percent was bioconvertable at 250°C. Overall soluble biodegradability was high at low temperatures, but decreased linearly with increasing temperature. Hence it appears that the effect of pretreatment on biodegradability is due to lysis of the cell and hydrolysis of the macromolecules into smaller and more degradable constituents. However, at higher temperatures these soluble constituents were converted to refractory compounds, and hence there are two competing mechanisms which result in an optimal biodegradability at around 175°C.

The addition of NaOH and HCl led to higher biodegradability, especially at the higher pretreatment temperatures, however, whether their addition is economically justifiable is not known. The addition of $Ca(OH)_2$ led to lower biodegradabilities as was found with earlier work on refuse.

Unfortunately thermochemical pretreatment also led to the production of toxic compounds, and this effect became more pronounced with temperature

increase, NaOH and HCl addition, and concentration of WAS. However, acclimation to these toxicants occurred quite quickly in a number of cases, and hence it may be possible to mitigate this problem with the use of acclimated populations.

D. FACTORS AFFECTING BIODEGRADABILITY

In the third phase of the study a number of hypotheses were addressed as to the cause of the refractory nature of the nitrogenous organic materials. These were the effect of long term biodegradability, the difference between mesophilic and thermophilic biodegradation, and the influence of oxygen. Data from long term (145 days) biodegradation tests indicated that most of the refractory compounds present were not transitory, and persisted over the long time period. However, some short term refractory compounds formed at high (250°C) pretreatment temperatures were degraded with increased time, and it appears that the microbial population used could acclimate to them.

Surprising differences were observed in overall bioconvertabilites between mesophilic and thermophilic conditions, and thermophilic populations resulted in significantly lower bioconvertabilities under all the conditions studied. Analytical techniques used (including the BMP assay) were examined closely, and it appears that the differences noted were real and not the result of analytical errors.

The presence or absence of oxygen in biodegradation tests appeared to have little effect either on overall biodegradabilities or on the individual nitrogen components studied, and hence it appears that the refractory nature of the nitrogen components studied was due primarily to molecular structure rather than to the presence or absence of oxygen.

E. PURE COMPONENT STUDIES

In the final phase the effect of thermochemical pretreatment on the

bioconvertability and toxicity of mixtures of pure nitrogen components (amino acids, proteins, purines and pyrimidines), and the pure components themselves were studied. With mixtures, all were found to be highly bioconvertable under mesophilic conditions, however, as noted previously, bioconvertability under thermophilic conditions was significantly lower. Pretreatment, with and without NaOH, at 200°C led to a decrease in bioconvertability in almost all cases, and the difference between mesophilic and thermophilic degradation was still apparent. Both DNA and the amino acid mixture were toxic at the high concentrations (20 g/l) tested, and pretreatment increased this toxicity in all cases. However, under thermophilic conditions in most cases, the pretreated mixtures were less toxic. The reason for this was not apparent from the data.

Most pure components tested were moderatley to highly bioconvertable, however, thermochemical pretreatment led to substantial decreases in almost all cases. Most pure components at the concentrations tested (20 g/l) were toxic, and thermochemical pretreatment rendered them even more so, even at quite low concentrations (1.3 g/l). While some correlation was noted between structure and bioconvertablity, for example the presence of branching or aromatic rings in amino acids functional groups lowered bioconvertability, it was concluded that prediction of biodegradability based on purely structural considerations was somewhat simplistic. A similar conclusion was drawn with regard to toxicity.

F. SUMMARY

From the data in this study it can be concluded that thermochemical pretreatment of nitrogenous organics present in bacterial cells can lead to substantial increases in biodegradability. The mechanism of action appears to be lysis of the cell followed by hydrolysis of the macromolecules to their more readily degraded constituents. As the pretreatment temperature rose, these

soluble constituents were converted to refractory compounds, and an optimum temperature was reached in the range of 175 to 200° C. Above this, biodegradability decreased with increasing temperature. Unfortunately, toxic compounds were also produced during pretreatment, their effect becoming more pronounced with temperature, NaOH and HCl addition, and solids concentration.

Both of these effects have important engineering implications in the design of processes to increase methane yield from refractory nitrogenous organics. It is recommended, in order to maximize methane yield from thermochemical pretreatment, that a heat treatment reactor be employed with a short hydraulic detention time, e.g. an upflow fluidized bed operated at low (150 to 175 C) temperatures. This would minimize the conversion of soluble degradable products of hydrolysis to refractory ones, and enable the effluent to be treated in more efficient anaerobic processes for dilute wastes as described under Section II. With constant removal of the soluble product, it is likely that the rate and extent of solids hydrolysis would also be enhanced. Finally such a process would tend to minimize the production of toxic compounds due to its relatively low operating temperature, and hence enhance process stability.

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Cornell University
College of Agriculture and Life Sciences
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Report Number COO-EY-S-02-2981-12

ANAEROBIC FERMENTATION OF AGRICULTURAL RESIDUES--POTENTIAL FOR IMPROVEMENT AND IMPLEMENTATION

Twelfth Quarter Progress Report for Period From
March 16, 1979 to June 15, 1979
Plus
Addendum Describing Project Activities From
June 16, 1979 to October 15, 1979
Plus
Addendum Progress Report No. 2 From
October 16, 1979 to January 15, 1980

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Prepared For
The U.S. Department of Energy
Under Contract No. EY-76-S-02-2981
Modification A002

Anaerobic Fermentation of Agricultural Residues--
Potential for Improvement and Implementation

Addendum Progress Report No. 2

October 16, 1979 to January 15, 1980
Cornell University, Ithaca, NY

PROJECT STATUS

During the period October 16, 1979, to January 15, 1980, the Cornell methane project continued work toward the completion of the tasks outlined in the work plan (Figure 8). Project planning and preliminary studies for the next phase of the methane project ("Low Cost Approach to Methane Generation, Storage, and Utilization from Crop and Animal Residues") scheduled to be funded January, 1980, were also conducted. This brief addendum will outline the accomplishments contributing to the progress of the project within this period.

Full Scale Plug Flow and Completely Mixed Reactors

The 25°C, 30-day HRT test condition was completed October 18, 1979. The steady state data for both fermentors are presented in Table 16. Steady state biogas production rates averaged 0.86 m^3/m^3 reactor-day with a TVS destruction efficiency of 28.1% for the complete mix reactor. As with the other conditions investigated the plug flow reactor exhibited superior performance, with steady state gas production rates averaging 0.93 m^3/m^3 reactor-day and a TVS destruction efficiency of 32.0%. Both fermentors produced gas that was 61% methane. At the lower operating temperature of 25°C (versus 35°C) both reactors exhibited increased sensitivity to temperature fluctuations. Reactor temperature variations of ±1°C were reflected in the daily gas production values.

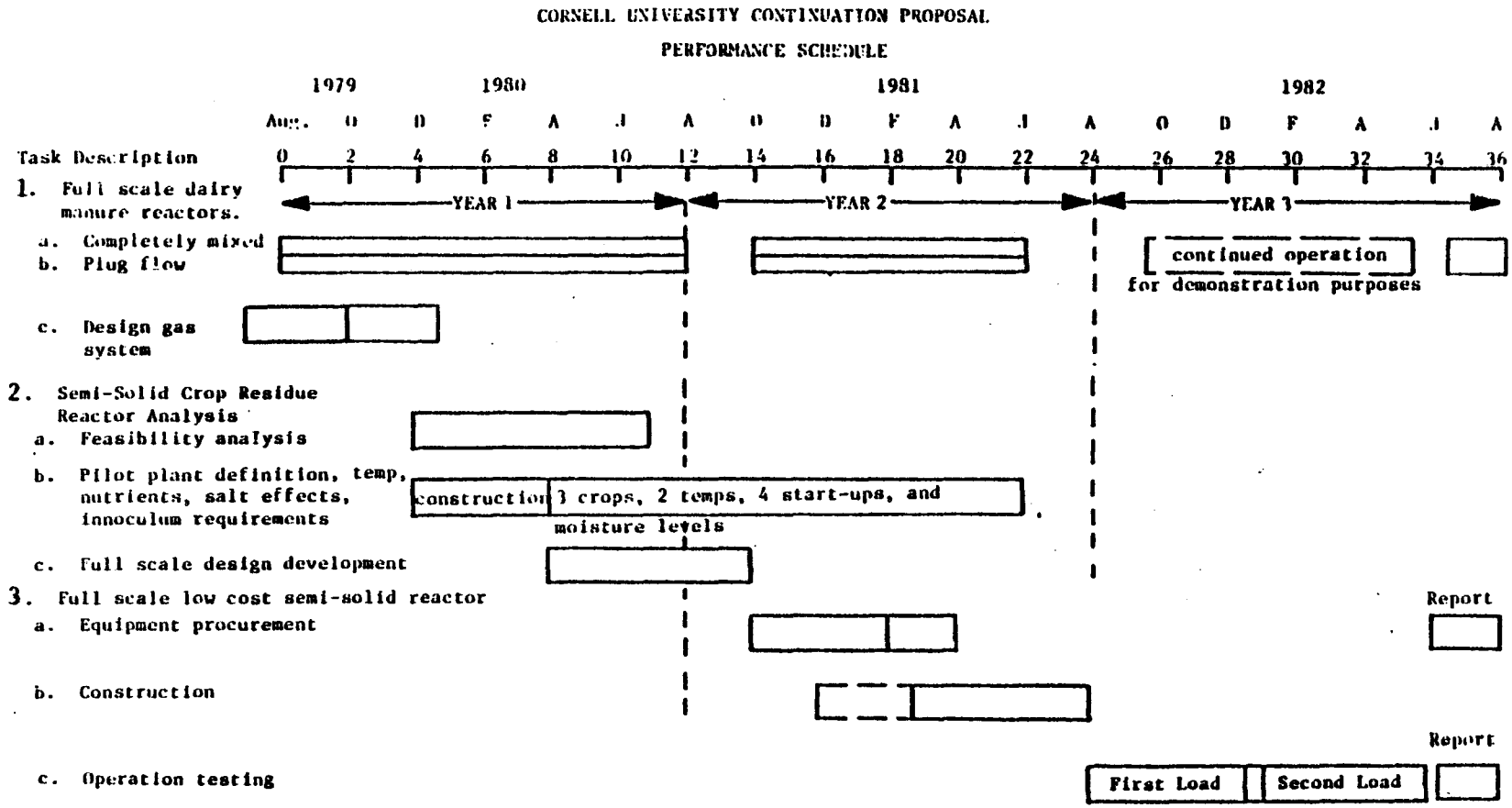


Figure 8. Schedule of tasks, events, and output of research and development program.

TABLE 16. STEADY STATE DATA (109 DAYS OF CONTINUOUS OPERATION) COLLECTED FROM THE FULL SCALE PLUG FLOW AND COMPLETELY MIXED REACTORS AT 25°C WITH A DESIGN HRT = 30 DAYS.

Reactor Type	HRT, days	Gas Production				Solids Destruction % TVS
		% CH_4	vol/vol	ℓ/gm VS_A	m^3/day	
Complete Mix	30.0	61	0.86	0.25	30.4	28.1
Plug Flow	29.2	61	0.93	0.26	37.2	32.0

Following the completion of the 25°C, 30-day HRT condition, the reactors were placed in a non-testing mode of operation, maintaining the 25°C, 30-day HRT while minor repairs and modifications were performed. One such modification was the addition of a gas scrubbing device for removal of H_2S from the biogas. A desire to decrease boiler down-time was the impetus for the gas scrubbing device(s). The device utilizes iron filings for the removal of H_2S with a copper sulfate indicator in the pressure control water trap to illustrate the effectiveness of the scrubber.

On January 2, 1980, the operating temperature of both full scale fermentors was raised from 25°C to 35°C. The new test condition will be 35°C at a 20-day HRT. Results of an economic evaluation have indicated that this condition would be in the optimal range for a dairy farm with 50 to 65 cows.

Pilot Scale Dry Fermentor

This unit has been operating for 427 days without the input of additional substrate. Gas production is 0.11 m^3/day with a methane content of 50%. The unit will soon be opened for physical inspection of the contents.

Final Report

The preparation of the final report continued during the period from October 16, 1979, to January 15, 1980. The text of the final report, with figures, illustrations, and tables is now in a completed rough draft form. It is anticipated that a final draft will be completed by February 15, 1980.

Feasibility Manual

With the majority of the manual text in draft form, the thermal loss/economic evaluation computer programs will be incorporated into a complete

package, with the manual to provide preliminary energy and economic information for specific farm operations. Using examples and worksheets in the manual, a farmer would be capable of calculating some of the basic data needed to determine the feasibility of incorporating an anaerobic digester into the overall farm management scheme. The computer program would take the specific information for each operation and evaluate potential net energy production, reduction of current energy consumption, and a basic financial outline, including capital investment, possible tax credits, and expected payback recovery periods.

NRAES Bulletin

This bulletin is near completion. With the addition of the graphics it will be ready for distribution by February 15, 1980.

Side Study Reports

Two reports, one entitled "Predicting Methane Fermentation Biodegradability" and the other entitled "Dry Anaerobic Fermentation to Methane of Organic Residues" are being readied for distribution by February 15, 1980. The first report is the M.S. thesis of J. A. Chandler, and the other report is the Ph.D. thesis of W. J. Wujcik.

Thermophilic Dry Fermentation Study

Due to the low moisture content of substrates undergoing dry fermentation, elevated temperatures may be achieved due to the production of waste heat during bacterial metabolism. Previous reports have shown that temperatures in the thermophilic range may be attained during dry fermentation. The objective of this study was to observe the gas production rates that could be achieved at thermophilic temperatures using a wheat straw substrate.

Gas Production Versus Substrate Initial TS Content--

In order to determine the effect of the initial TS content of the substrate on gas rate and composition, four 800 mℓ capacity reactors were placed in operation as described in Table 17. Each fermentor was filled with 40 grams of air dried wheat straw and seeded with effluent (cow manure) from a thermophilic seed fermentor. Using 1600 mℓ capacity gas displacement tubes, gas production and composition were monitored for 26 days.

The effect of initial TS content on cumulative methane production is shown in Figure 8. Fermentors at 15% and 21% initial TS contents showed a rapid rate of methane production and consequently substrate destruction. Fermentation for these two fermentors was essentially complete in 21 days. These data also suggest that a substantial drop in the rate of thermophilic wheat straw fermentation occurs somewhere between a solids content of 21% and 26%. Gas production and composition at initial TS contents over 26% could not be accurately measured due to the slow rate of fermentation observed.

Semi-Batch Thermophilic Dry Fermentation--

It was observed from the previously described batch study that complete fermentation of wheat straw at 20% initial TS content took place in less than 21 days. Furthermore, it was observed that 70% of the biodegradable volatile solids (BVS) could be degraded in approximately 7 days while maintaining a high rate of methane production. From these favorable results it was decided that a semi-batch mode of operation might be possible. Using a 5 ℓ capacity plexiglass reactor, a large quantity of wheat straw seed was established by first fermenting wheat straw using thermophilic (cow manure) fermentor effluent. Using this wheat straw seed as inoculum and a small amount of raw dairy cow manure as the source of nutrients, semi-batch thermophilic dry fermentation was initiated.

TABLE 17. BATCH THERMOPHILIC DRY FERMENTATION OF WHEAT STRAW.

Number of reactors:	4
Initial % TS:	15%, 21%, 26%, 31%
Temperature:	55°C
Seed TS/Feed TS:	0.10
Seed TKN/Feed TS:	0.005 g/g
Buffer/Feed TS:	0.066 g/g
Volume:	0.4 ℓ

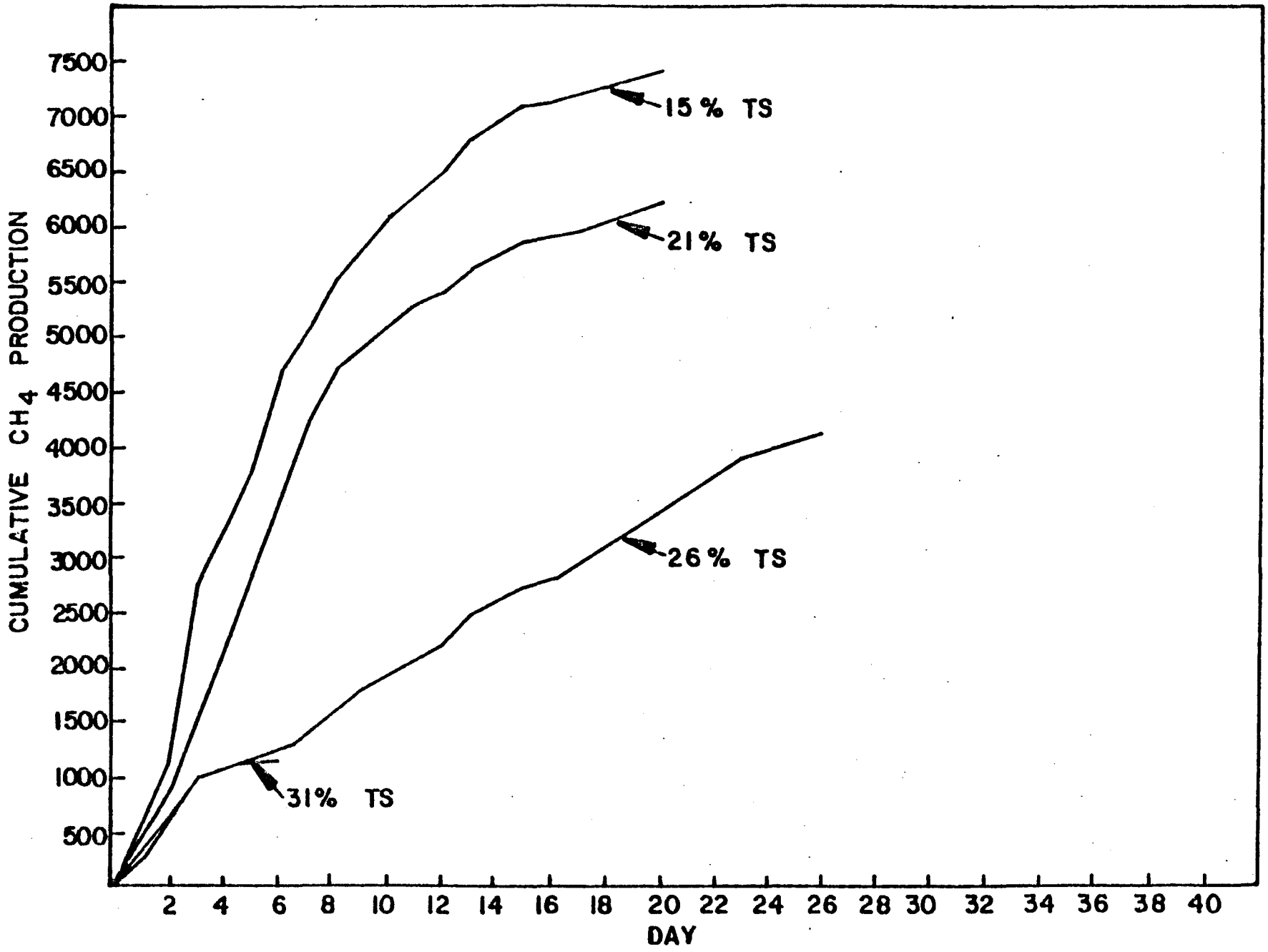


Figure 9. Thermophilic Batch Fermentation of Wheat Straw at 55°C

The operation of this semi-batch fermentor is described in Table 18. At the end of seven days the contents of the fermentor were emptied, except for a small quantity which was saved for use as seed. The fermentor was then refilled with wheat straw and dairy cow manure, and fermentation was allowed to continue another seven days.

Biogas and methane production for semi-batch operation is shown in Figure 9. Peak gas production occurs three to four days after feeding. The maximum biogas production attained by this unit equalled 6.8 vol/vol-day with a methane content of 49%. Table 19 is a summary of the semi-batch fermentation results. Very high biogas and methane yields were attained by this fermentor. However, only 53% BVS destruction was obtained instead of 70% as would be indicated by the previous batch fermentation study. This discrepancy is believed to be attributable to the difference in the size of fermentor used in these studies and consequently the ability to distribute free moisture within the fermentor.

The results of this preliminary study indicate that thermophilic dry fermentation is capable of producing large quantities of biogas in a relatively short period of time. However, several questions in regards to both full scale system performance and feasibility cannot be answered at this time. Further work on thermophilic dry fermentation will be undertaken during the upcoming dry fermentation study.

FUTURE ACTIVITIES

Full Scale Dairy Fermentor Systems

Preliminary evaluation of the two-year full scale testing program has indicated that operation at 35°C and a 20-day HRT may yield an optimal balance of biogas production versus capital investment and recovery. This operating

TABLE 18. OPERATION OF SEMI-BATCH THERMOPHILIC DRY FERMENTATION OF WHEAT STRAW

Initial % TS	19.8%
Temperature	55°C
SRT	7 days
Seed TS/Feed TS	0.10 g/g
Cow Manure TKN/Feed TS	0.006 g/g
Buffer[1]/Feed TS	0.082 g/g
Volume	≈ 3.5 ℓ

1: Supplied as $NaHCO_3$

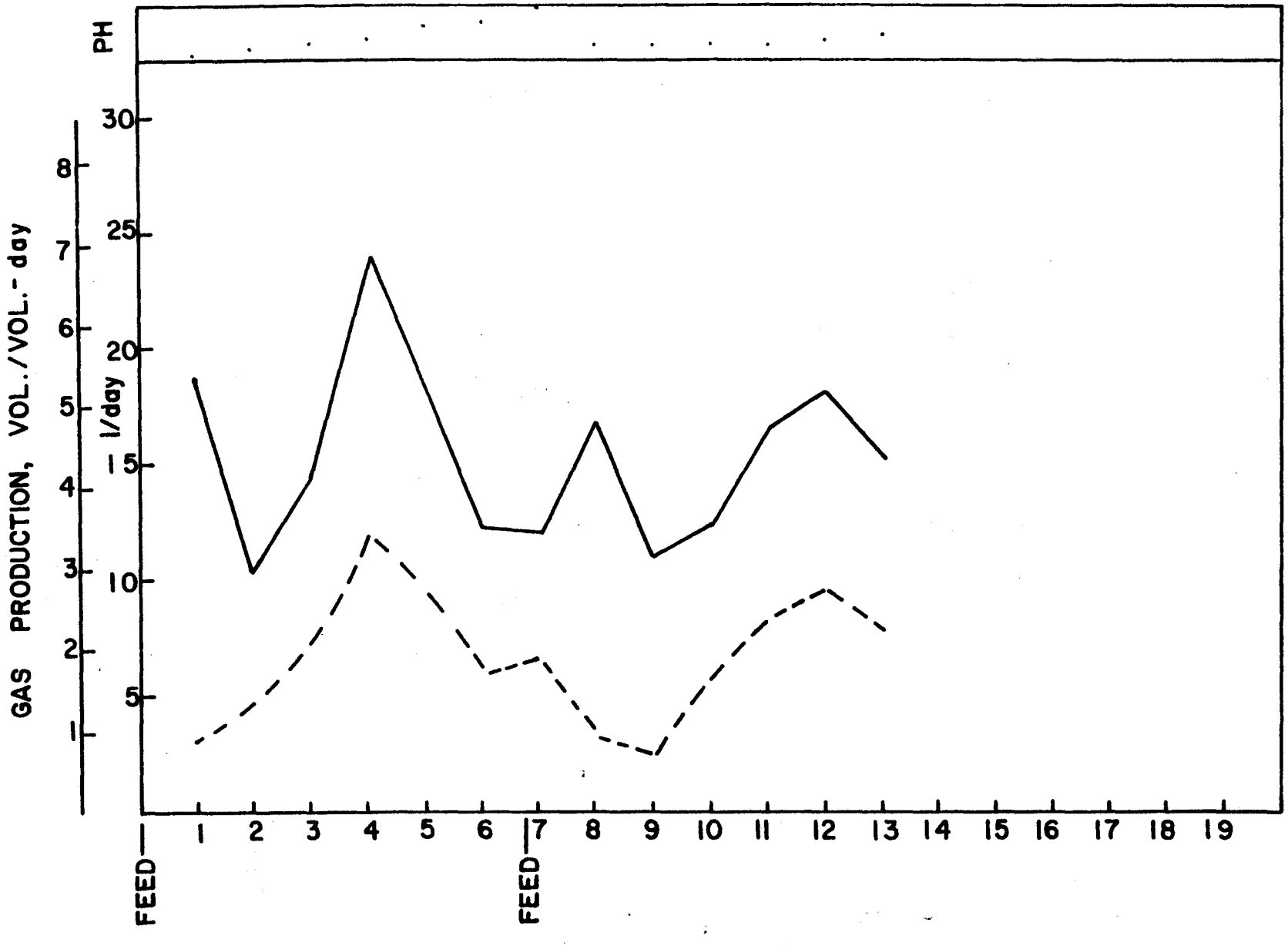


Figure 10. Biogas and Methane Production for a Semi-Batch Operated Thermophilic Operated Wheat Straw Fermentor.

TABLE 19. RESULTS OF THERMOPHILIC SEMI-BATCH DRY FERMENTATION STUDY.

Average Biogas Production	4.4 vol/vol-day
Average CH_4 Production	1.8 vol/vol-day
Maximum CH_4/CO_2	60/40
% VS_D grav	30.6%
% VS_D gas[1]	26.2%
% VS_D gas/% VS_D grav	0.86
mℓ $CH_4/_g VS_A$	115
mℓ $CH_4/_g VS_D$	375
% BVS_D[2]	52.6%
Final % TS	15.7%

[1]Assuming COD/VS = 1.25, 0.350 ℓ CH_4/g COD_D

[2]Estimated from composite wheat straw-cow manure VS $lignin_s$ content

condition will therefore be maintained for a 12-month period to allow a more detailed energy assessment to be performed on a seasonal basis. Continued operation of the plug flow and completely mixed reactors will also provide additional time to evaluate the basic design and the performance of the materials used in its construction.

Gas Utilization

Due to the uncertainty of funding for the gas utilization study, no permanent modifications of the existing systems will be undertaken. However, a preliminary assessment of the potential for biogas utilization at the Cornell dairy facility will be performed. This brief study will consider how the gas may be used, what portion of current energy costs may be recovered, and what physical modifications are necessary to retrofit the existing system.

Dry Fermentation Study

The proposed dry fermentation laboratory study will be conducted in three stages. Phase I will investigate system start-up and operation. This will include the effects of seed, nutrients, substrate biodegradability, and composition on start-up. The effect of free moisture recirculation on the rate of biogas production will also be observed. The bench scale study will then lead to start-up of two pilot scale dry fermentors evaluating the effects of bulk density. Thermodynamic studies will be conducted on all pilot scale reactors. Phase I will also serve to acquaint the personnel with procedures of operation, establish analytical techniques, and test the computer data retrieval system.

Phase II will continue the bench scale studies in areas of dry fermentation kinetics in mixed-phase and separated-phase reactors. Techniques of separating the phases will be developed. Tests will be performed to investigate

various sources and quantities of buffering. As with Phase I, the results from this bench scale study will lead to the start-up of additional pilot scale reactors.

Phase III will be flexible to allow further bench scale studies as found necessary during Phases I and II. Phase III may include thermodynamic, alternative substrate, and thermophilic studies.

A feasibility report to assess the potential of community-scale dry fermentation will be an ongoing task. Included in this report will be topics such as:

1. feasibility of fermentor operation modes;
2. material handling and transportation;
3. effluent utilization and cooperative industrial development;
4. fermentor management;
5. environmental and social considerations;
6. identification of optimum community fermentor system design.

A detailed engineering design will be generated from the optimal community system identified in the feasibility study.

An outline of the proposed tasks for the first year of study is presented in Figure 11.

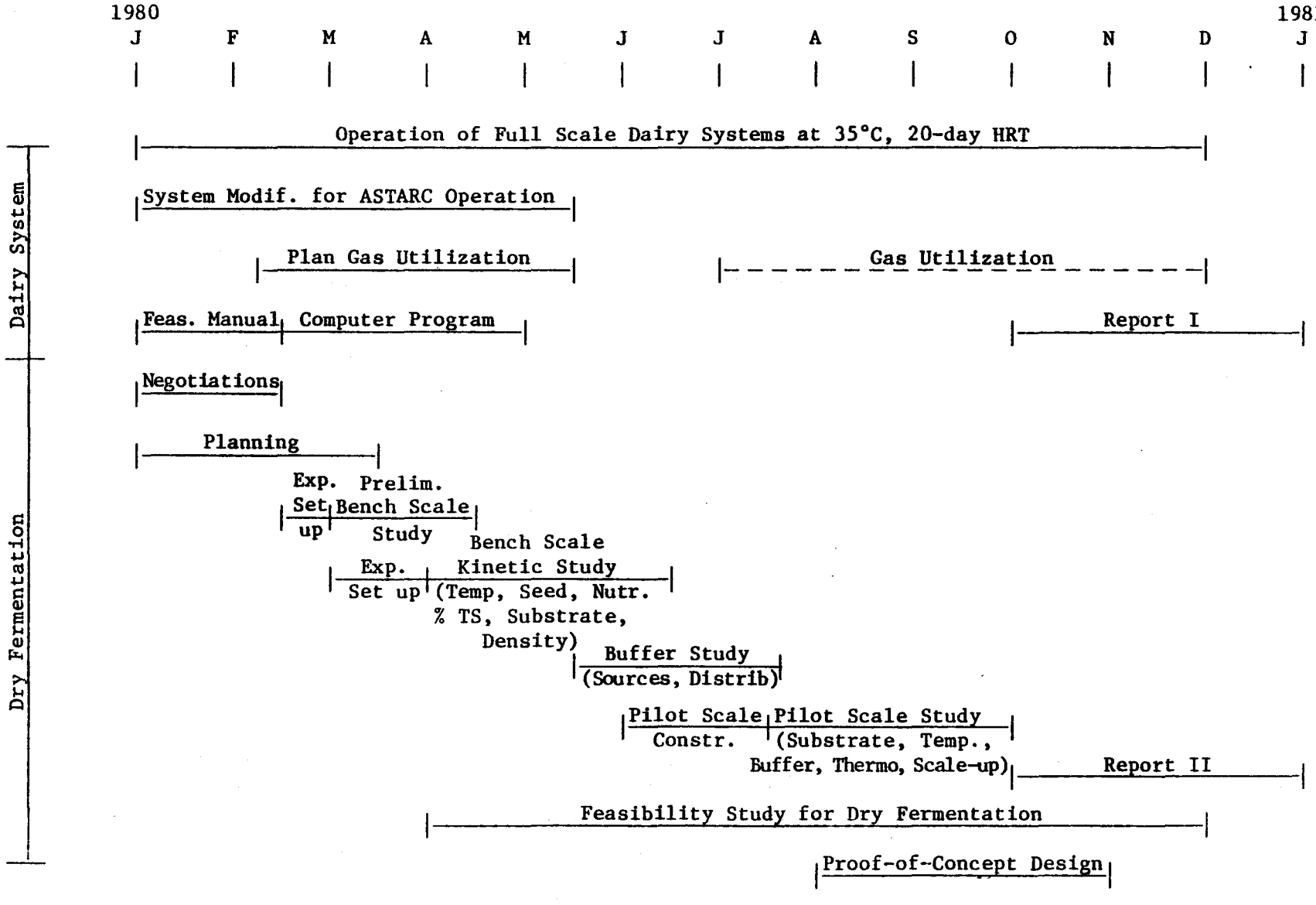


Figure 11. Projected schedule of tasks, events, and output of research and development program for the first year.

HAMILTON STANDARD Division of UNITED TECHNOLOGIES

FUEL GAS FROM AN ENVIRONMENTAL FEEDLOT

CONTRACT NO EG-7-C-01-4015

PROGRESS FROM SEPTEMBER 30, 1979 TO DECEMBER 31, 1979

PREPARED FOR THE

QUARTERLY COORDINATION MEETING

JANUARY 30 - FEBRUARY 1, 1980

SUMMARY

Operation of the experimental fermentation facility at Kaplan Industries in Bartow, Florida during 1979 yielded data on a range of retention times from 20 to 10 days. Most of this data was obtained at an operating temperature of 55°C (131°F). The data is considered preliminary because long term equilibrium in the fermentors was not reached. One conclusion of the testing to date is that specific methane yields are not as high as were obtained in prior test programs conducted by Hamilton Standard in the laboratory and the field with fresh cattle residues. This is most likely caused by the presence of Rumensin in the cattle diet.

Product gas was successfully utilized in the system boiler and co-fired with oil in the meat packing plant boiler. Work continued on the grid-connected generator package.

FERMENTOR PERFORMANCE AT 50°C (122°F)

During the period of time when fermentor #2 was operated at 122°F, retention times of 40, 26.7 and 20 days were utilized as a means of bringing the fermentation on line. Gas production was below the threshold of the 4" gas meter during the 122°F testing; however, the gas flow was measured during the 20 day retention period by closing the gas outlet valve and recording pressure rise during loading. This method only yields data over a short time span and also suffers from other secondary errors such as gas solubility and temperature stability. The resultant average specific methane production for the 20 day case was 3.67 cu ft of methane per pound of volatile solids loaded (cu ft/lb vs). The standard deviation for this data was 3.01 cu ft/lb vs. This wide variation was in part artificially caused by large variations in the daily volatile solids loading. (This period of operation occured during the normal rainy season and there were large daily variations in the residue concentration). One more important point is that the data is not representative of an equilibrium condition. The fermentor was at the 20 day level for only 14 days. During this time the solids concentrations was continually increasing in the fermentor.

FERMENTOR PERFORMANCE AT 55°C (131°F)

At the 55°C operating temperature, data was accumulated at retention times of 20, 18.2, 14, and 10 days. In every case there was enough gas production to allow use of the 4" gas meter. Two sets of data are available at the 20 day retention time, one from fermentor #1 and one from fermentor #2. The specific methane production averaged 3.15 and 3.02 cu ft/lb vs respectively with standard deviations of 1.37 and .93. Of all the data presented, the 20 day data is most representative of steady state conditions. Towards the end of this period, the solids concentration in the fermentors nearly achieved a steady value. Prior to this period, fermentor #1 was at a 10 day retention time. The average specific methane production for this condition was 2.63 cu ft/lb vs with a standard deviation of .68. Prior to this, the fermentor was at a 14 day retention time for a short period of only 12 days. During this time, specific methane production averaged 2.71 cu ft/lb vs with a standard deviation of 1.19. The longest single period of testing occurred before the 14 day retention time segment. During this time, covering 59 days, the retention time was 18.2 days. The specific methane production averaged 3.66 cu ft/lb vs with a standard deviation of 1.59. During the 18.2, 14 and 10 day retention times period, the dry matter of contents of fermentor #1 steadily increased from 2.74% to 5.72%.

PERFORMANCE CONCLUSIONS

Comparing the data for all the 55°C operation to the Dynatech model for a continuously stirred tank reactor reveals a non-biodegradeable portion of the organic material of approximately 49.3%. This is much higher than the 22% obtained from data prior to the use of Rumensin. However, the effects of Rumensin require more definitive evaluation before the cause for lower performance can be definitely identified.

PRODUCT UTILIZATION

Product gas utilization in the system boiler was continued successfully. The Kaplan Industries meat packing plant boiler was successfully co-fired with oil and product gas for a short period of time with product gas at a rate of 1 MMBTU per hour. Continued use in the Kaplan Boiler was limited due to boiler problems not associated with the gas supply.

The design and assembly for the control console for the engine generator is proceeding as planned. The engine supplier went out on strike in October 1979 and returned to work in January 1980 with a resultant significant delay in the delivery of the engine generator. It is expected that the total package will be completely assembled on site by the end of April 1980.

- Performance History
- Process Performance
- System Performance
- Boiler Utilization
- Engine/Generator
- Future Plans

PERFORMANCE HISTORY

- Feb. 79 → Initial Start Up (131°F)
  - Process Problems
    - TVA
    - pH
    - Inhibition
  - System Problems

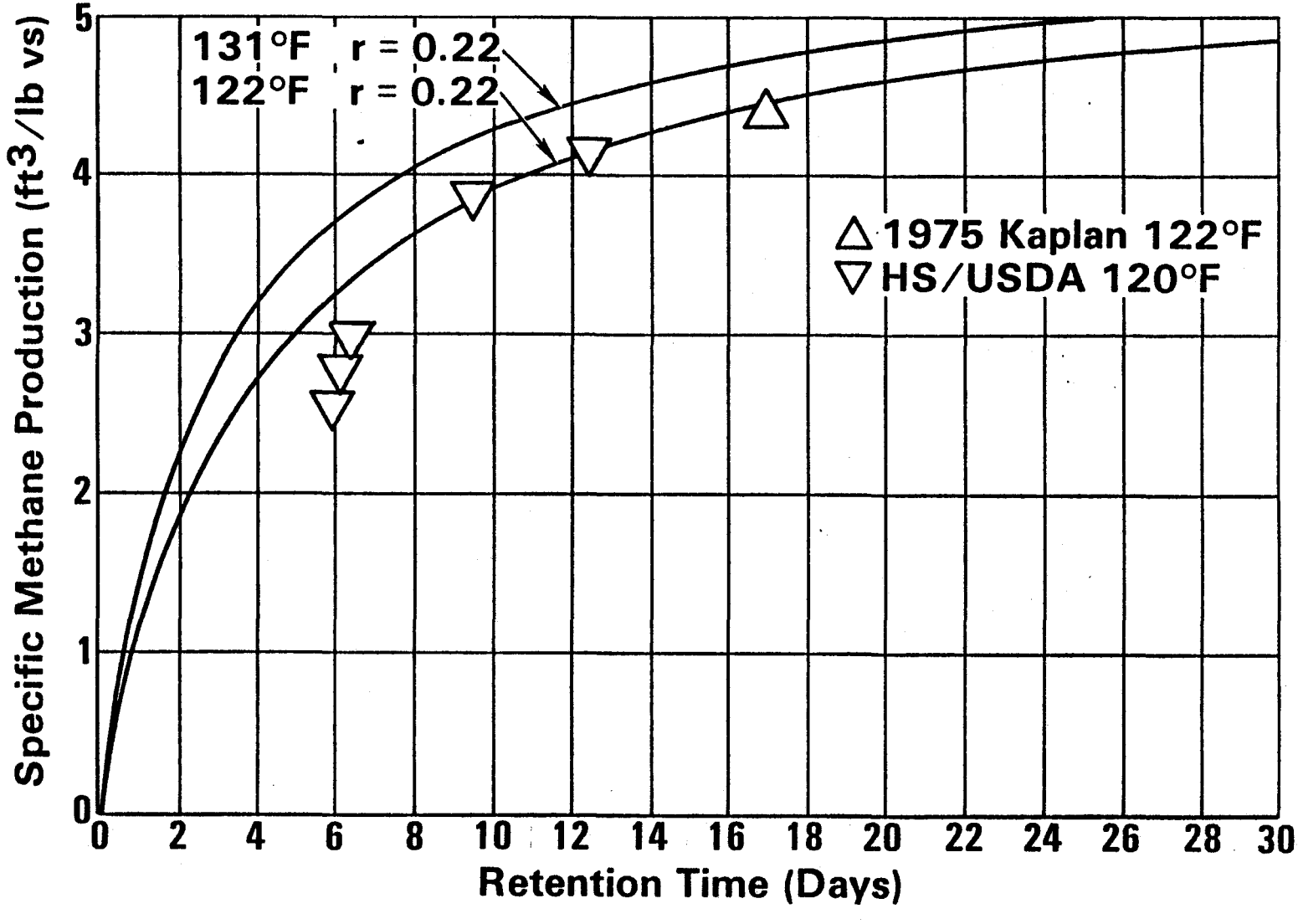
- May 79 → Second Start Up (122°F)
  - Successful
  - Shut Down for Mechanical Work

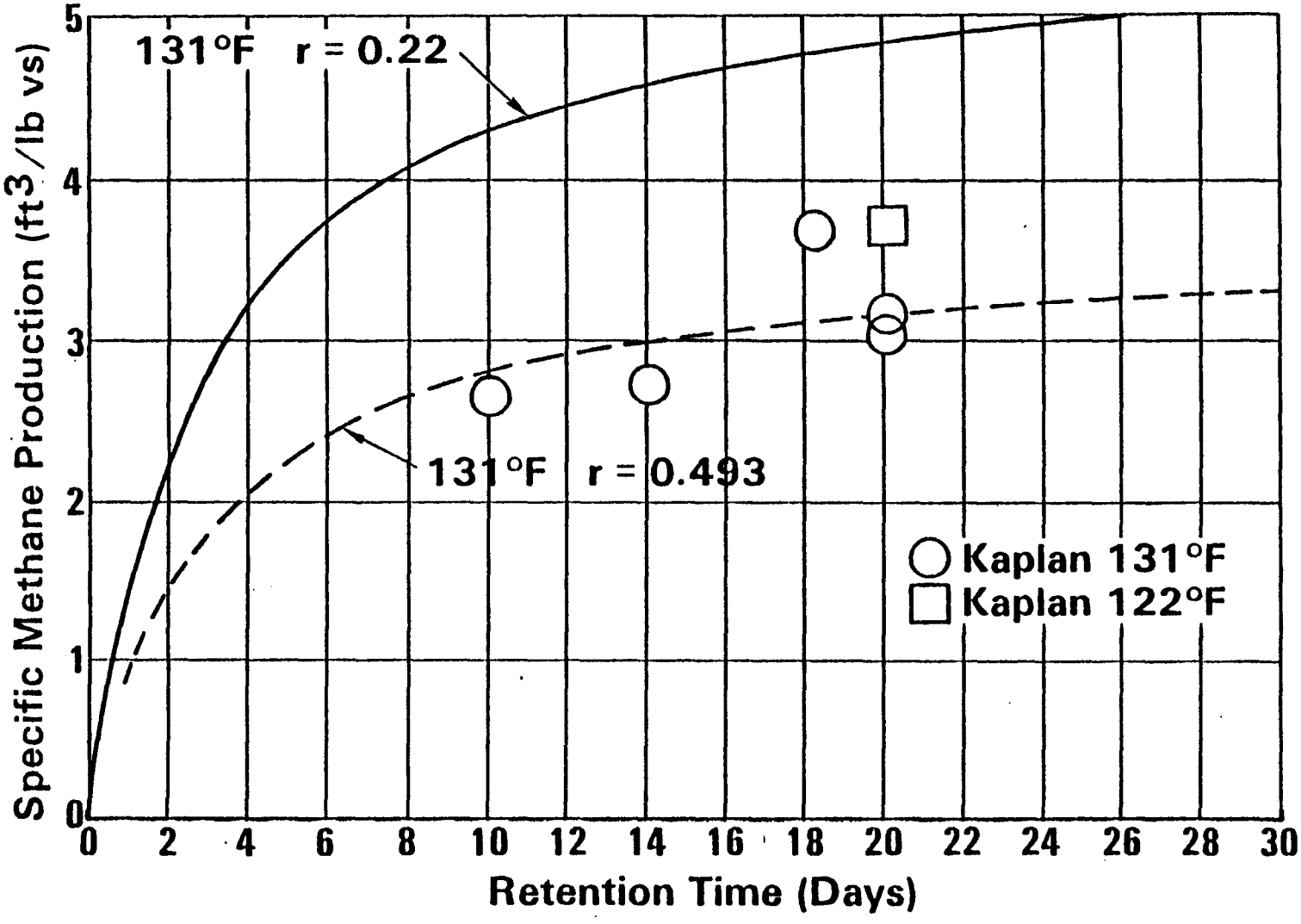
- June 79 → Third Start Up (131°F) (Still Operating)

PROCESS PERFORMANCE

OPERATING CONDITIONS SUMMARY

Retention Time (Days)	Fermentor	Temperature (°F)	Residue Volatile Solids (%)	Fermentor Dry Matter (%)	Time at Condition (Days)	Time Order
20	2	122	4.66	2.44	14	1
20	2	131	7.34	5.32	31	5
20	1	131	7.04	6.07	46	5
18.2	1	131	3.96	2.89	59	2
14	1	131	4.19	2.81	12	3
10	1	131	6.16	4.53	27	4


131°F r = 0.22
122°F r = 0.22
△ 1975 Kaplan 122°F
▽ HS/USDA 120°F
Specific Methane Production (ft3/lb vs)
Retention Time (Days)
0
1
2
3
4
5
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30


131°F r = 0.22
131°F r = 0.493
Kaplan 131°F
Kaplan 122°F
Specific Methane Production (ft3/lb vs)
Retention Time (Days)
0
1
2
3
4
5
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30

POSSIBLE CAUSES OF LOW PRODUCTION

- Inhibition
- Characteristics of Residue
- Variability in Loading
- Insufficient Time at Conditions

SYSTEM PERFORMANCE

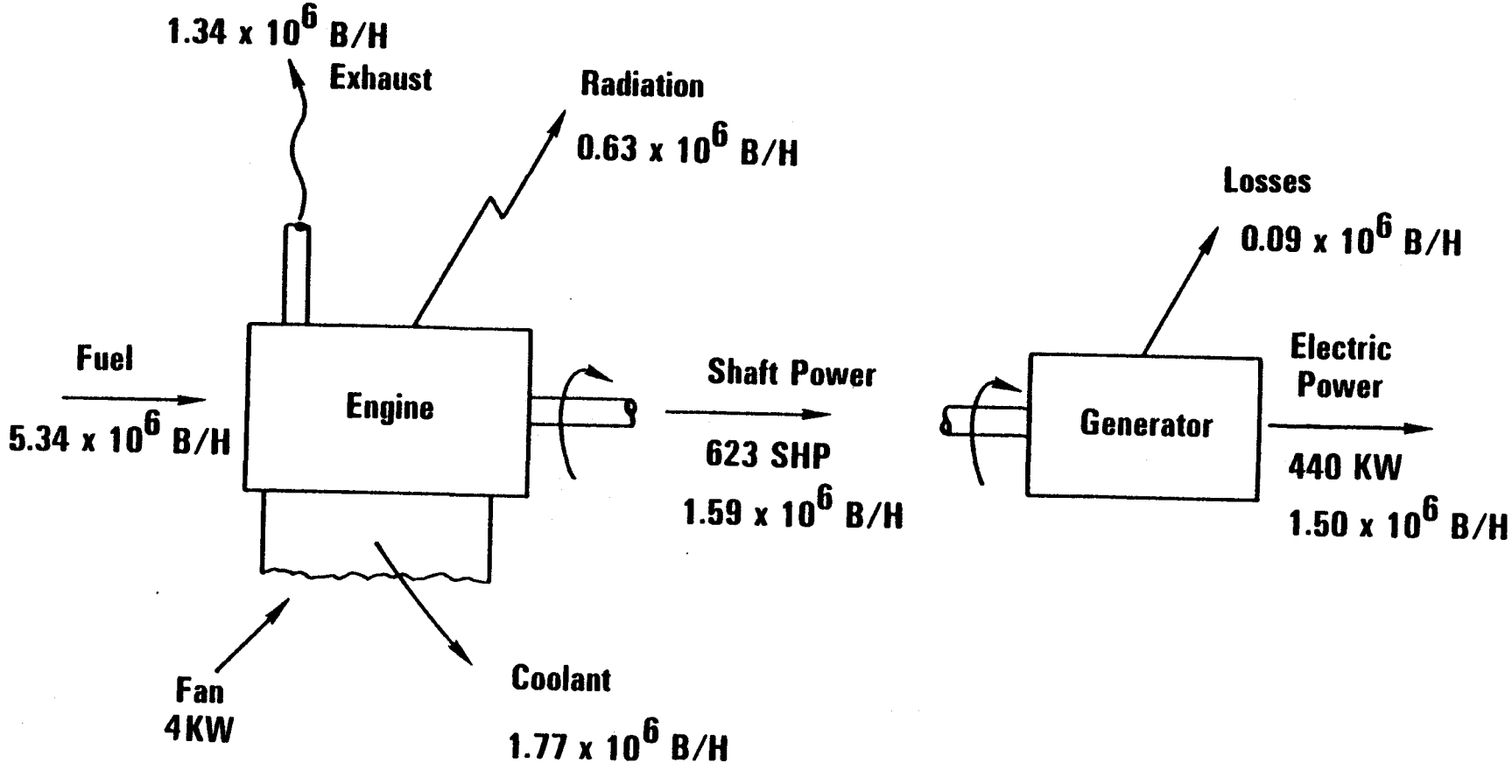
DESIGN CHANGES

Problem	Change
Temperature Control	Eliminated Tank Direct Temperature Control
Level Sensing	Plan to Install Pressure Sensing Level Gages
Residue Supply Lines	Increased Pipe Size
Comminutor	Open
Withdrawal Pump	Open
Blower	Open

Concept Changes — None

- Engine
- Generator
- Controls

ENGINE GENERATOR ENERGY BALANCE



FEATURES

Utilizes Fermentor Gas
Provides 440 KW
Continuous Duty
Coolant Heat Recovery
Efficient

Fuel Supply Matching
Synchronization
Protective Relaying
Reactive Power Control

Advantages

- Increased Utilization of Dispersed Non Conventional Energy Sources
- Increased Capacity of Feeder
- Improved Feeder Power Efficiency

Disadvantages

- Increased Feeder Fault Currents
- Complicates Substation Breaker Reclosure
- Increased Hazard to Personnel

PROTECTIVE RELAYING

Generator	Feeder	Engine
Internal Short	Over Current	Low Oil Pressure
Loss of Field	Loss of Phase	High Water Temp
Short to Ground	Under Voltage	Overspeed
	Over Voltage	Low Water Level
	Under Frequency	Low Fuel Pressure

NUTRITIONAL STIMULATION OF METHANE BACTERIA

Quarterly Report - Jan. 1980

Gene Parkin
R. E. Speece
Drexel University

Commonly the limiting step that controls the maximum rate of loading with anaerobic digestion is the conversion of acetate to methane gas by methanogenic bacteria. In addition, acetate is the precursor to approximately 70% of the methane produced in the anaerobic digestion of complex organics. The methanogenic bacteria converting acetate to methane are, therefore, critical. The objective of this study is to assay a number of selected organic and inorganic compounds for possible stimulation of acetate utilizing methanogens.

This initial quarter of the project has been devoted to development of procedure for assay of methanogenic stimulation. The methanogens are an acetate-enriched culture maintained in our laboratory for over four years on a chemically defined medium with acetate as the sole energy-carbon source (exclusive of 10 mg/l of cysteine). Two approaches have been taken to assay stimulation. The first approach utilizes the Hungate serum bottle technique, modified by McCarty. The second approach involves construction of a Nutristat which is a modification of a similar concept proposed by Bungay.

The serum bottle assay involves the placement of a chemically defined medium into a serum bottle that contains an anaerobic environment with a color indicator for ORP. An innoculum of acetate-enriched menthanogens cultured on the aforementioned chemically defined medium is anaerobically transferred to the serum bottle. Finally, the substance to be assayed is injected and 10,000 mg/l of calcium acetate is added. It has been verified that this concentration of calcium acetate is not toxic when injected as a slug.

The gas production, which is 100% methane, is recorded daily and compared with a control. The pH is maintained at close to 7 under all conditions by the use of calcium acetate even though the head gas is 100% methane.

The Nutristat is a continually stirred reactor with feedback control. The gas production is metered and triggers a feed pump that stoichiometrically adds the amount of acetic acid which was converted to the volume of gas recorded by the gas meter. Thus, the concentration of acetate within the reactor is relatively constant and independent of the utilization rate. Substances to be assayed are added to the reactor and the change in gas production rate over the background rate is taken as the measure of stimulation.

Variability among the controls in the assay procedure is excessive and the transfer technique is being scrutinized. Preliminary assays of individual (no combinations yet) vitamins, amino acids and complex sources of trace organics are being conducted. Stimulation is defined as gas production that is two standard deviations above the average of the controls. Preliminary data indicates that 0.2 mg/l of folic acid, 0.09 mg/l of vitamin B_6 and 0.001 mg/l of vitamin B_{12} are stimulatory according to this definition when added individually. It is significant that higher and lower concentrations of these vitamins were not stimulatory. Yeast extract at 1000 mg/l is quite stimulatory

BIOMETHANATION OF BIOMASS PYROLYSIS GASES

Technical Progress Report #1

Period Covered:

November 1, 1979 to January 31, 1980

Subcontract No. XB-9-8356-1
Dynatech Project No. SLR-5
Dynatech Report No. 1988

Submitted to:

Dan Jantzen
Bio/Chemical Conversion Branch
Solar Energy Research Institute
1536 Cole Boulevard
Golden, CO 80401

Prepared by:

L. R. Moschini

January 31, 1980

BIOMETHANATION OF BIOMASS PYROLYSIS

The work to be completed under this contract, No. XB-9-8356-1, at Dynatech Corporation consists of optimizing and maximizing the yields from biological processes for converting gasifier gases to methane. Other work will demonstrate that a biological process for methanation can be conducted with gases containing carbon monoxide and will evaluate the effects of actual gasifier gases on the processes. Finally, the data from the experimental program will be applied to improve upon previous engineering analysis and economic evaluations.

This report relates the progress made through the first three months of the 13-month contract. Progress was very limited during November and December 1979 due to the late receipt (January 1980) of the contract. Without the contract, spending was limited to $10,000. This funding was insufficient to permit ordering and purchasing of any equipment. However, during January all major equipment orders were placed. All items required for the initial start-up will be available by mid-February. This should permit the experimental program to begin on March 1, 1980.

The contractual period of performance for the program is 13 months. The delay in contract receipt effectively delayed progress approximately one month. By starting on March 1, 1980, the program can be completed by November 30, 1980 but there is no "buffer" month to absorb delays, if any.

In addition to the ordering of equipment, laboratory space was selected and a design was drawn up specifying the required alterations.

The experimental program is outlined below according to tasks, each with a summary of performance scheme to be undertaken.

Task 1: Optimization of Shift Conversion Reaction

A 2-liter agitated pressure reactor has been ordered from Pressure Products Industries (PPI). The microorganisms required, a Rhodopseudomonas culture, will be obtained at the appropriate time. It is anticipated that the reactor will operate for four months under mesophilic conditions and then be operated for four more months under thermophilic conditions. During each four-month period the microorganisms culture will first be brought up to its maximum population (and gas output) under atmospheric conditions. Once this level has been established through appropriate nutrient feed and biomass recycle, the reactor pressure will be gradually increased. Cell population and gas productivity will be monitored and promoted to maximum.

Task 2: Maximization of Methanation Reaction Rate

Another 2-liter agitated pressure reactor will be utilized for the methanation study. A culture of Methanogens is being maintained at Dynatech and will be available for this study. As with the shift reaction study, it is anticipated that the methanation reactor will be operated for four months under mesophilic conditions and for four months under thermophilic conditions. After the culture has been maximized under atmospheric conditions, the reactor will be gradually elevated in pressure to 1,000 psig.

Two pressure boosters from Haskel Engineering Corp. have been ordered to permit full utilization of the supply gas cylinders for both high pressure reactors.

Task 3: Demonstration of Combined Shift Conversion and Methanation

Two atmospheric reactors will be utilized for this demonstration. A New Brunswick Fermenter has been allocated from previous contract equipment and will be used for the thermophilic mode. A 2-liter Pyrex kettle

will be used for the mesophilic mode. For both cases the initial approach will be to introduce a low percentage of CO into the feed gas. The culture will be mixed, with the majority Methanogens, the minority Rhodopseudomonas. If the mixed culture stabilizes at some compatible population level, then increased CO levels will be attempted to determine what feed gas ratios can be accommodated. In any event the microorganism population will be repeatedly evaluated to determine what alterations, if any, it develops. This will also aid in determining nutrient optimization and recycle methods.

Task 4: Determination of Effects of Biomass Gasifier Gases on Microorganisms

This task is still being defined. The assistance of Mr. Ray Desrosiers from SERI has been obtained to help in the design and specification of a small-scale gasifier utilizing wood pellets as the feedstock. The current plan calls for setting up four small flask reactors, two at mesophilic conditions and two at thermophilic conditions. All four reactors will be brought to a steady state methane output with bottled gases. Then two of the reactors will be subjected to a period of continuous gasifier feed, while methane output and other parameters are evaluated.

Task 5: Conduct Supportive Analytical Tests

All equipment to support the analytical test program is either in house or on order. A comprehensive outline of the test procedures is now being prepared.

ACKNOWLEDGEMENTS

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Mr. Carl A. Tracy	Experimental expertise